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NATURE OF THE MgO and Al_2O_3 CONDUCTIVITY

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ABSTRACT

The conductivity of MgO and Al_2O_3 is determined at 1500-1700°C. It is found that at this temperature MgO has almost entirely ion conductivity. Al_2O_3 is a combined conductor with the electron conductivity comprising about 25%.

A study of the conductivity of extremely fireproof oxide materials is of great theoretical and practical value. It is well known that at ordinary room temperatures, oxides are good insulators (Ref. 1). However, many oxides become electric current conductors with a temperature increase. /42*

The conductivity of solid oxide materials at 1500-1700°C is very important with respect to the extensive studies on the development of galvanic concentration cells, which are used to determine the activity of the main components of metallurgical melts (Ref. 2-4). Solid oxides are frequently used as solid electrolytes in these cells.

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*Note: Numbers in the margin indicate pagination in the original foreign text.

It is well known that all materials which can conduct an electric current can be conditionally divided into three groups:

(1) Conductors with electron conductivity (of the metallic or semi-conductor type n or p);

(2) Conductors with ion conductivity (dielectrics);

(3) Combined conductors - with electron and ion conductivity.

The relationship between the electron and ion conductivity in combined conductors depends on the temperature change and on their chemical composition.

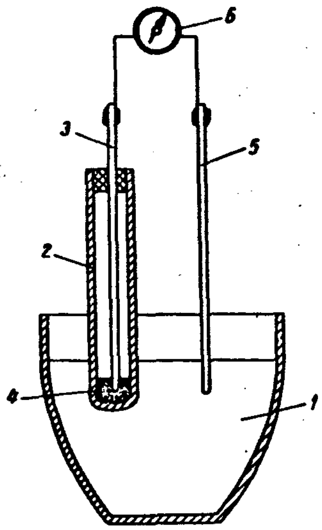
One important feature of dielectrics and of semi-conductors is the existence of admixture (low-temperature) and natural (high-temperature) conductivity. The change from admixture conductivity to natural conductivity occurs between 800-1200°C for MgO and Al_2O_3 (Ref. 5, 6).

The majority of studies have investigated the conductivity of solid oxides at high temperatures by measuring the transport number in ion conductors. The study (Ref. 7) determined that the conductivity of magnesium oxide monocrystals is purely ionic in nature at 1100°C.

At 1300°C the portion of electron conductivity in pellets prepared from pure magnesium oxide was 15-17% in all (Ref. 8).

In order to clarify the conductivity of the solid oxides MgO and Al_2O_3 at high temperatures, we employed baked magnesium oxide and baked corundum, prepared by the Pozol'skiy Factory of Fireproof Products. The oxides were employed as solid electrolytes in a galvanic concentration cell (see the figure). The characteristics of the oxides are presented in the table.

A cell of the following type was constructed:



Drawing of the Oxide Test

1 - Metal to be studied; 2 - MgO or Al_2O_3;
3 - Graphite; 4 - Cast iron; 5 - Tungsten;
6 - Measurement device.

Fe-O-C || MgO or Al_2O_3 || Fe-O-C saturated.

OXIDE CHARACTERISTICS

Material	Chemical Composition, %						Apparent Density (Volumetric Weight) g/cm^3	Apparent Porosity %
	SiO_2	Al_2O_3	TiO_2	CaO	MgO	R_2O		
Baked magnesium oxide	0.72	-	-	0.18	98.42	0.42	3.25-3.30	0-1.0
Baked corundum	0.45	98.0	0.8	0.25	0.23	0.38	3.85	0-1.5

The electromotive force (e. m. f) of this cell was determined by the equation of Nernst: /43

$$E_T = \frac{RT}{nF} \ln \frac{a_B}{a_{0\,(c)}}, \tag{1}$$

where: n - the transport number of the process determining the potential;

a_B - oxygen activity in the melt being studied, which is determined by the vacuum smelting data.

$a_{0(c)}$ - oxygen activity in the comparison electrodes, determined from preliminary experiments;

R - gas constant;

F - Faraday number;

T - absolute temperature.

The experimental smelting was performed in a resistance furnace with a graphite heater. About 400 g pure iron were melted in a fireproof crucible. The oxygen activity changed with respect to the smelting process in the melt being studied. The metal temperature was measured by a PR 30/6 platinic rhodium-platinum thermocouple.

After a constant temperature was reached, a fireproof cover with cast iron poured into it, which served as the electrode of comparison, was introduced into the melt. The emf produced in the given concentration cell was measured when the tungsten bar was periodically dipped into the metal. In order to guarantee the reversible operation of the galvanic cell, the emf was measured by a compensation method, employing a high-resistance PPTV-1 potentiometer and a mirror galvanometer with a sensitivity of one division per 10^{-9} a. The oxygen activity in the comparison electrode, which had been established previously (Ref. 3), remained constant at 0.0004.

Equation (1) can be written as follows:

$$E_\Phi = \frac{1{,}98 \cdot T \cdot 2{,}3 \cdot 10^3}{n_\Phi \cdot 23\,000} \lg \frac{a_B}{a_{0\,(c)}} = \frac{1{,}98T}{n_\Phi} 10^{-1} \lg \frac{a_B}{a_{0\,(c)}} \text{ mv} \qquad (2)$$

where n_{Φ} - transport number of the process determining the potential in a combined (electron and ion) conductor;

$$\text{or } E_{\Phi} = K_{cp} \cdot \lg \frac{a_{n}}{a_{0\,(c)}} \text{mv}, \qquad \text{where } K_{cp} = \frac{1{,}98T}{n_{\Phi}} 10^{-1}. \tag{3}$$

When MgO was used as the solid electrolyte, the measurements were performed at 1600°C (1870°K). Consequently,

$$K_{cp} = \frac{1{,}98 \cdot 187}{n_{\Phi}}. \tag{4}$$

Based on the results for 15 measurements, the magnitude of K_{cp} is 176; Thus, $n_{\Phi} = 2.07$.

It is well known that if the solid electrolyte has an ion and electron conductivity of the n or p type, then the emf in the concentration galvanic circuit is determined by the equation of Wagner (Ref. 9):

$$E_{\Phi} = E_{T}(1 - n_{э}), \tag{5}$$

where E_{Φ} is the measured emf;

E_{T} - the emf calculated thermodynamically;

$n_{э}$ - the electron transport number (portion of electron conductivity).

Consequently, we have

$$\frac{E_{\Phi}}{E_{T}} = (1 - n_{э}) = \frac{n_{T}}{n_{\Phi}}. \tag{6}$$

According to our experimental data, for MgO this relationship equals

$$\frac{n_{T}}{n_{\Phi}} = \frac{2{,}0}{2{,}07} = 0{,}97.$$

Consequently, $n_{э} = 0.03$.

Thus, the portion of electron conductivity for MgO is 3% in all at 1600°C. Taking the low accuracy of these calculations into account, we can assume that

MgO has almost entirely ion conductivity.

In the second series of experiments, we determined the conductivity of Al_2O_3 at 1600 and 1650°C. All of the computations were performed in the same way as for MgO.

Based on the results of 30 measurements, the K_{cp} for Al_2O_3 is 137 at 1600°C, and 145 at 1650°C. At these temperatures, the magnitude of n_{Φ} is 2.82 and 2.63, respectively, for Al_2O_3. Equation (5) was used to calculate the portion of electron conductivity in Al_2O_3, assuming that $n_T = 2$, due to the fact that $Al_2O_3 = 2Al^{3+} + 3O^{2-}$.

The electron transport number for Al_2O_3 equalled: $n_э = 0.29$ at 1600°C and $n_э = 0.24$ at 1650°C.

Consequently, the portion of electron conductivity in Al_2O_3 is significant; it decreases with an increase in temperature, which was observed previously (Ref. 8).

A recorder to determine the state of oxidation of the liquid metal based /44 on the smelting process, the output, and the casting was produced, based on the concentration galvanic cell which had been developed and tested.

A knowledge of the oxygen activity (content) in the smelt opens up wide possibilities for controlling the productive process, and makes it possible to significantly influence the quality of the metal, which greatly depends on the oxygen content.

Conclusions

The conductivity of Mgo and Al_2O_3, employed as the solid electrolyte at temperatures which are characteristic of steel production processes, was determined by means of a concentration galvanic cell.

At these temperatures, MgO had almost entirely ion conductivity.

Al_2O_3 is a combined conductor. The portion of electron conductivity in it is about 25%, and it decreases with a temperature increase.

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